

Technical Status Report No. 6

CHEMISTRY OF THE ATMOSPHERE
OF THE PLANET VENUS

Rensselaer Polytechnic Institute
Troy, New York

1 February 1965 - 31 July 1965

Research Grant No. NSG-261/33-18-007

R.P.I. Project 441.68

FACILITY FORM 602	N 65 88438	
	(ACCESSION NUMBER)	(THRU)
	66	done
	(PAGES)	(CODE)
	CR-67264	
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

P. Harteck

R. R. Reeves, Jr.

and

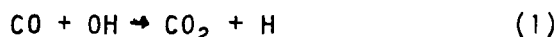
Barbara A. Thompson

CHEMISTRY OF THE ATMOSPHERE OF THE PLANET VENUS

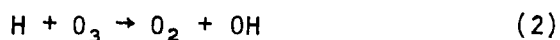
Photochemistry with Bromine Lamp

Photochemical equilibrium studies using the bromine lamp which emits the 1633 Å persistent line of bromine have continued with particular reference to CO_2 . When pure CO_2 was irradiated dissociation could readily be observed with formation of CO and O_2 , O_3 was also present and the O_3/O_2 ratio was comparable to that obtained with pure O_2 . The CO: O_2 ratio was determined mass spectrometrically (O_3 decomposes to O_2 in the mass spectrometer), and found to be 2:1. This is in contrast to the results of some who have reported finding less than the stoichiometric amount of oxygen. The position of the dissociation equilibrium seemed to be somewhat variable, the maximum equilibrium value for CO/CO_2 being ~ 0.3 ($\text{O}_2/\text{CO}_2 \sim 0.15$). To try to establish the equilibrium position better, irradiations were made of mixtures of CO, O_2 , and argon. In every case reaction to form CO_2 proceeded to completion. When excess CO was present, all the O_2 was consumed; when excess O_2 was present, all the CO was consumed. Close examination of the mass spectra revealed the presence of trace amounts ($\sim 0.1\%$) of water vapor. Experiments were then carried out in which the reaction gases were dried with extreme care. When this was done the equilibrium was shifted slightly in the direction of increased dissociation ($\text{O}_2/\text{CO}_2 \sim 0.03$) indicating that the water vapor was catalyzing the recombination reaction. The fact that no higher degree of dissociation was obtained starting with CO - O_2 mixtures could be explained by the purification procedures used. CO_2 was obtained very dry

(Coleman grade) and was further dried by low temperature distillation. CO was purified from small amounts of iron carbonyl by bubbling through sodium hydroxide solution and then drying through liquid oxygen traps. As a result of these procedures the CO, even after careful drying through a series of liquid O₂ traps, undoubtedly contained substantially higher amounts of water than the CO₂. The recombination most probably takes place via the reaction:



since OH radicals and H-atoms are present as photodissociation products of water. The OH radicals can be regenerated in several ways, most likely by reaction with O₃:



As a check on the mechanism a series of irradiations was carried out on pure CO₂ to which traces of H₂ had been added. The H₂ molecules should react with O-atoms to form OH radicals and, if the proposed mechanism is correct, inhibit the CO₂ dissociation. It was found that with 0.1% H₂ the dissociation of CO₂ was completely inhibited (O₂/CO₂ < 0.005). With 0.01% H₂ a small amount of dissociation occurred (O₂/CO₂ ~ 0.02). Thus the proposed mechanism appears to be correct. It should be noted that most of the added hydrogen remained in the form of H₂ as could be observed mass spectrometrically and only a small fraction was converted to H₂O during the time of irradiation. Whether the dissociation maximum of CO/CO₂ ~ 0.3 found with pure CO₂ represents a trace residue of water or a true equilibrium between CO₂, CO, O₂, and O₃ is uncertain at this point.

These results can explain the peculiar composition of the Venus atmosphere, i.e., a high abundance of CO_2 with no more than a trace of either CO or O_2 . These constituents might be expected to be present in the Venus atmosphere in relatively high concentrations due to photodissociation of CO_2 . The most recent spectroscopic investigations from a balloon carried out by Strong and his group at Johns Hopkins seem to indicate the presence of trace amounts of atmospheric water vapor. For the above mechanism involving Reactions (1) and (2) only small amounts of water need be present. Photodissociation of the water would produce OH radicals and H -atoms which could be expected to be present in steady-state down to the cloud layer. It seems probable, therefore, that any oxygen or carbon monoxide formed in the Venus atmosphere react to regenerate carbon dioxide in the manner described above.

Irradiations of O_2 with traces of H_2 have been carried out to determine whether similar factors might be responsible for the unexpected results previously obtained for the $\text{O}_2 - \text{O}_3$ equilibrium. It was found that with 0.01% H_2 the equilibrium O_3/O_2 ratio was substantially reduced from 0.26 to 0.18. With 0.1% H_2 the ratio was reduced to 0.05. Thus it can be concluded that even more stringent controls of purity are required than had been thought in order to obtain meaningful results.

Photochemistry with Iodine Lamp

Dr. Galli has carried out a series of irradiations of acetylenic hydrocarbons using the iodine lamp and is now putting his results in a form suitable for publication. Copies of the work will be forwarded to NASA when preparation for publication has been completed.

CO + O-Atom Reaction

Studies have continued on this reaction. The work performed in the spring gave results with somewhat larger scatter than expected when the rate coefficients were calculated on the basis of a simple two body homogeneous gas phase reaction. Additional data are now being obtained including results with various third bodies such as helium. Other variables are also being considered. It is clear that such reactions as those described earlier ($\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$; $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$) could effect the results, but no such interferences have been isolated as yet.

Microwave Emission Studies

Experiments have been carried out to determine optimum conditions for observation of microwave spectra emitted from glow discharges in CO_2 and SO_2 . Several spectra have been obtained and work in this area is continuing. Evaluation of the significance of the observations is being particularly stressed.

Publications and Presentations

A paper entitled "The Bromine Lamp: Studies of the Oxygen-Ozone and Carbon Dioxide Equilibria" by B. A. Thompson, R. R. Reeves, Jr. and P. Harteck was presented at the ACS Meeting in Detroit in April 1965. This paper has been accepted for publication in "The Journal of Physical Chemistry" and is scheduled to appear in the December 1965 issue. Copies of this paper have been forwarded to NASA.

A paper entitled "Radiation Equilibria Pertinent to Planetary Atmospheres" by P. Harteck, R. R. Reeves, Jr. and B. A. Thompson was presented at the symposium on atmospheric chemistry at Visby, Sweden in August 1965.

6.5.

A paper entitled "Photochemical Equilibrium Studies with CO₂" by R. R. Reeves, Jr. , P. Harteck and B. A. Thompson is scheduled for presentation at the ACS Meeting in Atlantic City in September, 1965 and will be submitted for publication in the next few weeks. Copies will be forwarded to NASA when completed.